Acknowledgment. I thank Dr. A. J. Paine for GPC measurements, Dr. K. Sienicki for fluorescence decay measurements, and Professor M. A. Winnik for the use of the SPEX fluorescence spectrometer in his laboratory and for many stimulating discussions.

Registry No. HPC, 9004-64-2.

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Two-Dimensional NMR of Polysaccharides: Spectral Assignments of Cellulose Triesters

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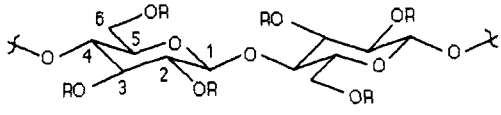
ABSTRACT: The combined use of homonuclear and heteronuclear two-dimensional NMR has provided the first unambiguous spectral assignment for the polymer backbone of cellulose triacetate, cellulose tripropionate, and cellulose tributyrate. Simple techniques have been applied which allow enhancement of the resolution in the one-dimensional spectra of these polysaccharides. Data are presented which suggest that the solution macromolecular conformation for cellulose esters is sensitive to both solvent polarity and size of acyl substituent.

Introduction

In the past 10 years, NMR techniques have routinely been applied to the study of cellulose esters.[1] In all of these reports, spectral assignments were made by chemical derivatization or by comparison to spectra of mono- or oligosaccharides. Moreover, due to line broadening and small differences in chemical shifts, much of the information potentially available from coupling patterns was lost. As part of our work in cellulose esters, we required unambiguous spectral assignments and simple techniques for improving resolution in one-dimensional (1D) spectra. The work presented here has provided complete spectral assignments for the polymer backbone of cellulose triacetate (CTA, **1**), cellulose tripropionate (CTP, **2**), and cellulose tributyrate (CTB, **3**). We have also found that in many cases, significant spectral enhancement can be obtained in the 1D spectra by application of a Lorentzian to Gaussian transformation with a suitable weighting constant. The data suggest that the solution macromolecular conformation of cellulose esters is sensitive to both solvent polarity and size of acyl substituent.



1 R = OAc
2 R = OPr
3 R = OBu

Results and Discussion

Chemical Shift Assignments. In analogy to the methods developed for NMR studies of oligosaccharides,[2] peptides,[3] and other polymeric systems,[4] an effective strategy for shift assignments of polysaccharides is through two-dimensional (2D) homonuclear and heteronuclear chemical shift correlation spectroscopy. The method allows assignment of proton resonances from the evidence of proton–proton connectivities which are then correlated with the resonances in the carbon-13 NMR spectrum. This process is demonstrated for CTA (1) ($CDCl_3$).

Figure 1a shows the 1D ^1H NMR spectrum of the ring region of CTA (1), to which resolution enhancement has been applied (vide infra). The coupling information contained in this spectrum and the ^1H–^1H connectivities in the homonuclear chemical shift correlation spectrum (COSY, Figure 2) permitted a straightforward assignment of the proton spectrum of CTA (1).

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Table I
^{1}H NMR Chemical Shifts and Coupling Constants[a] for CTA, CTP, and CTB

	CTA			CTP	CTB
	DMSO-d_6, 25 °C	DMSO-d_6, 80 °C	$CDCl_3$, 25 °C	$CDCl_3$, 25 °C	$CDCl_3$, 25 °C
H-1	4.65 (d, $^3J_{1,2}$ = 7.9 Hz)	4.65 (d, $^3J_{1,2}$ = 7.9 Hz)	4.42 (d, $^3J_{1,2}$ = 7.9 Hz)	4.35 (d, $^3J_{1,2}$ = 7.9 Hz)	4.34 (d, $^3J_{1,2}$ = 7.9 Hz)
H-2	4.52 (t, J = 7.3 Hz)	4.55 (t, J = 8.6 Hz)	4.79 (t, J = 8.6 Hz)	4.77 (t, J = 8.6 Hz)	4.76 (t, J = 8.6 Hz)
H-3	5.06 (t, J = 9.2 Hz)	5.04 (t, J = 9.2 Hz)	5.07 (t, J = 9.0 Hz)	5.07 (t, J = 9.1 Hz)	5.06 (t, J = 9.2 Hz)
H-4	3.65 (t, J = 9.2 Hz)	3.68 (t, J = 9.2 Hz)	3.71 (t, J = 9.2 Hz)	3.66 (t, J = 9.1 Hz)	3.61 (t, J = 9.2 Hz)
H-5	3.81 (m)	3.77 (m)	3.53 (m)	3.47 (m)	3.48 (m)
H-6$_S$	4.22 (d, $^2J_{6S,6R}$ = 10 Hz)	4.26 (d, $^2J_{6S,6R}$ = 11 Hz)	*b*	*b*	*b*
H-6$_R$	3.98 (m)	4.04 (m)	4.06 (m)	4.03 (m)	4.03 (m)

[a] Digital resolution was 0.20–0.26 Hz. [b] H-6$_R$ overlaps with H-1.

Table II
^{13}C NMR Chemical Shifts and Coupling Constants[a] for CTA, CTP, and CTB

	CTA		CTP	CTB
	DMSO-d_6, 90 °C	$CDCl_3$, 25 °C	$CDCl_3$, 25 °C	$CDCl_3$, 25 °C
C-1	99.8 (d, J = 167 Hz)	100.4 (d, J = 165 Hz)	100.3 (d, J = 163 Hz)	100.1 (d, J = 163 Hz)
C-2	72.2 (d, J = 152 Hz)	71.7 (d, J = 153 Hz)	71.7 (d, J = 150 Hz)	71.4 (d, J = 150 Hz)
C-3	72.9 (d, J = 151 Hz)	72.5 (d, J = 148 Hz)	72.2 (d, J = 148 Hz)	71.8 (d, J = 147 Hz)
C-4	76.4 (d, J = 151 Hz)	76.0 (b)	75.8 (d, J = 153 Hz)	75.8 (b)
C-5	72.5 (d, J = 146 Hz)	72.7 (d, J = 139 Hz)	73.0 (d, J = 138 Hz)	73.1 (d, J = 143 Hz)
C-6	62.8 (t, J = 151 Hz)	61.9 (t, J = 151 Hz)	61.9 (t, J = 147 Hz)	61.9 (t, J = 145 Hz)

[a] The digital resolution was 0.52 Hz. [b] The coupled resonance overlaps with the solvent peaks.

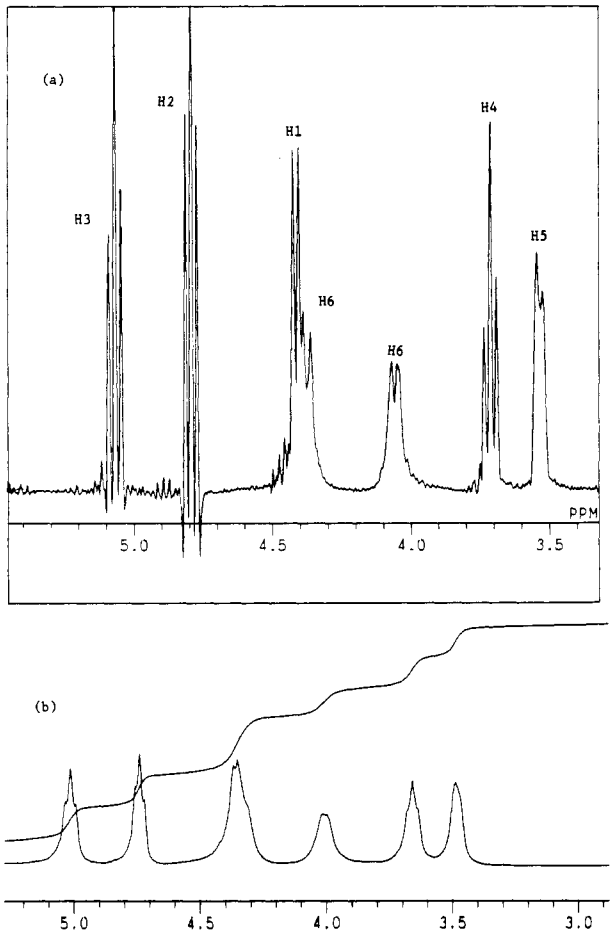

Figure 1. (a) CTA ($CDCl_3$, 25 °C, 128 acquisitions, pulse delay of 5 s) spectrum processed by using a Lorentzian to Gaussian transformation of the time domain FID. (b) CTA ($CDCl_3$, 25 °C, eight acquisitions, pulse delay of 5 s) spectrum processed using a Lorentzian transformation of the time domain FID.

Having assigned the resonances of the ring protons, assignment of the carbon spectrum was made by using 2D heteronuclear chemical shift correlation spectroscopy. Figure 3 shows the C–H chemical shift correlated spectrum for CTA (1), in which each methine group shows only one

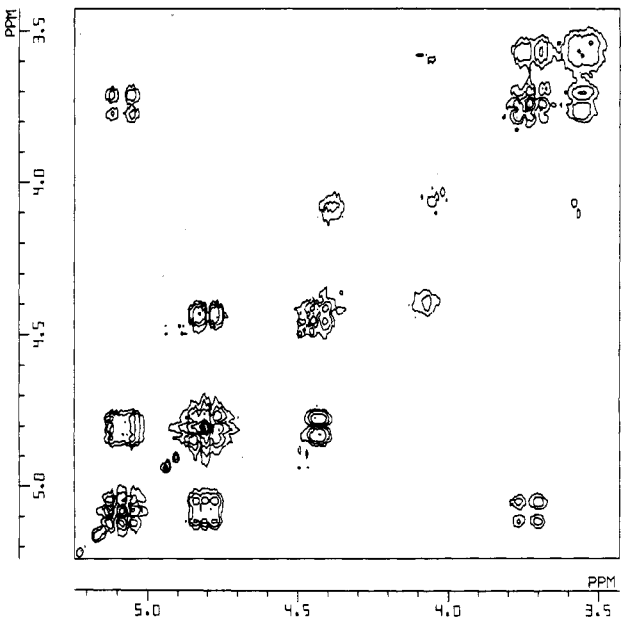

Figure 2. COSY spectrum of CTA ($CDCl_3$, 25 °C).

cross-peak. Although the methylene cross-peak for C-6 is absent, complete assignment of the ^{13}C spectrum can be made since C-6 is the only missing peak (this cross-peak is observed when the solvent is DMSO-d_6).

Having established the ^{1}H and ^{13}C NMR assignments for CTA (1) in $CDCl_3$, the same experimental protocol was followed in assigning the spectra of CTP (2) ($CDCl_3$), CTB (3) ($CDCl_3$), and CTA in DMSO-d_6. These results are tabulated in Tables I and II.

Couplings. As previously noted, the spectra of cellulose esters frequently do not provide all of the potentially available information due to poor spectral resolution.[5] Gagnaire, Taravel and Vignon[1f] recognized this limitation and applied 2D homonuclear J-resolved spectroscopy to the ^{1}H NMR spectrum of CTA (1). Although this provided the desired results, we required a technique less demanding of instrument time and hence applicable to large numbers of samples.

In 1966, Ernst[6] reviewed a number of methods designed for the enhancement of sensitivity and resolution in NMR

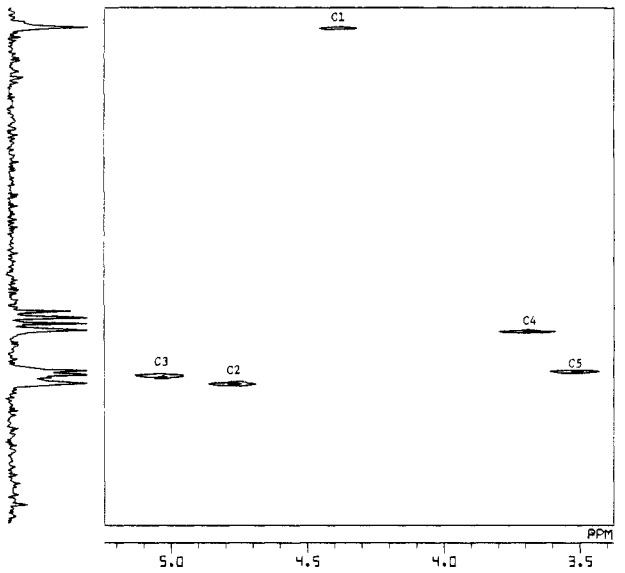

Figure 3. C–H heteronuclear chemical shift correlation spectrum of CTA ($CDCl_3$, 25 °C).

spectroscopy. One of the simplest of these methods is a Lorentzian to Gaussian transformation.[7] Pending proper selection of parameter values, this method provides a simple means for narrowing spectral lines, particularly in those cases in which line broadening is due to T_2 relaxation. Figure 1b provides the normal ^1H FT spectrum of CTA (**1**) (400 MHz, $CDCl_3$, 25 °C). The signals are broad and convey little spin–spin coupling information. However, by applying resolution-enhancement techniques to the time domain spectrum, the resolution is significantly improved (Figure 1a). While the normal ^1H NMR spectrum shows very poorly resolved triplets for H-2, H-3, and H-4, the corresponding enhanced spectrum provides cleanly resolved triplets. Similarly, the resonances of H-1 and H-6 (*pro-S*)[5] are overlapping in Figure 1b but are well-resolved doublets in Figure 1a as are the resonances for H-6 (*pro-R*) and H-5. Further enhancement (Figure 4a) shows that the signals for H-6_R and H-5, due to second-order effects, are actually complex multiplets.[8,9] Significantly, the resonance for H-6_S remains a simple doublet. Under these conditions any coupling between H-6_S and H-5 must be less than the observed line width (<1 Hz).

The ^1H and ^{13}C coupling constant data for CTP (**2**) ($CDCl_3$), CTB (**3**) ($CDCl_3$), and CTA (**1**) (DMSO-d_6), listed in Tables I and II, were determined in a similar fashion. Many features of the geometry of these polymers are evident from these data. Examination of the coupling constant data between vicinal protons indicates that they are of the magnitude, ca. 9 Hz, expected for β-D-glucopyranosyl residues in a $^4C_1$ conformation, although the smaller value for the H-1, H-2 coupling, $^3J_{H\text{-}1,H\text{-}2}$ = 7.9 Hz, suggests that there may be a flattening or twist at the anomeric center. The multiplicity of the resonances for the H-6_R protons does not permit accurate determination of coupling constants. However, the observed splitting for *H*-6_R of the triesters and the small coupling between the H-6_S and the H-5 protons indicate a preference exists in the rotamer population about the exocyclic C_6–C_5 bond. In agreement with Perlin[5] we find that, in all cases, the RCS rotamer (Figure 5) must be contributing heavily in solution whereas the contribution by the ROS rotamer must be minimal.

The most striking feature of the data from Table I is that the choice of the acyl group, solvent, or temperature had little or no effect on the magnitude of the proton vicinal coupling, and therefore on ring conformation,

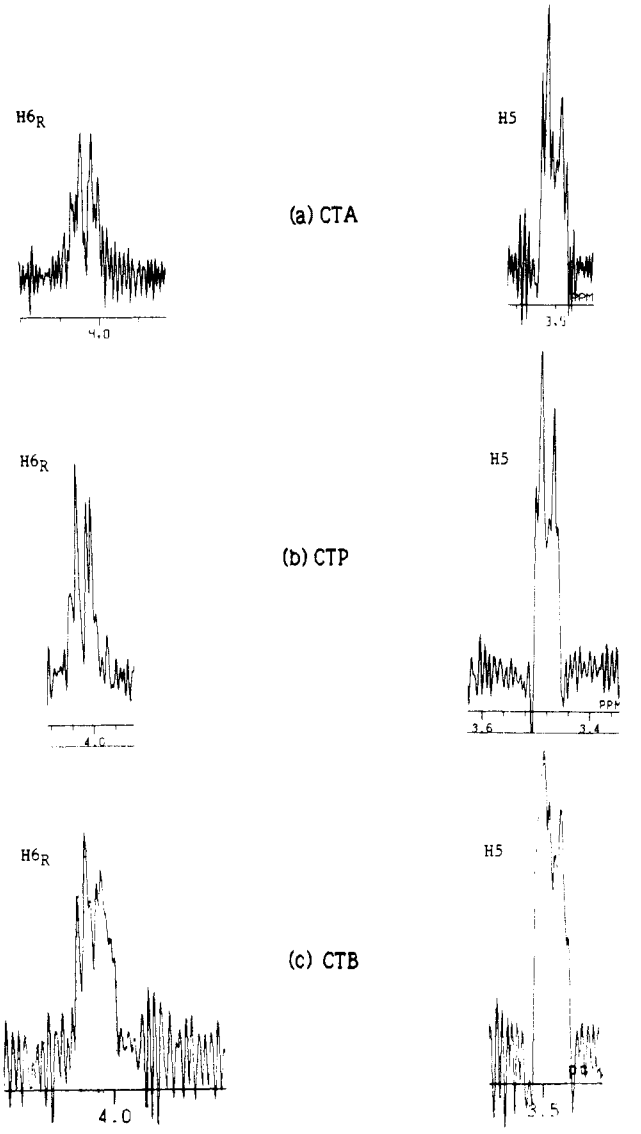

Figure 4. Resolution enhanced resonances for H6_R and H5 of (a) CTA, (b) CTP, and (c) CTB.

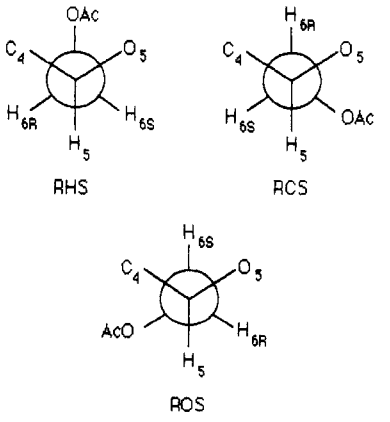

Figure 5.

whereas the chemical shifts were in many cases significantly affected by such changes. For example, changing the solvent from $CDCl_3$ to the more polar solvent, DMSO-d_6, resulted in a downfield shift (deshielding effect) for H-1 and H-5 and an upfield shift (shielding effect) for H-2. Increasing the temperature from 25 to 80 °C (DMSO-d_6) had only minimal effects on chemical shifts. Conversely, when the size of the acyl group was increased

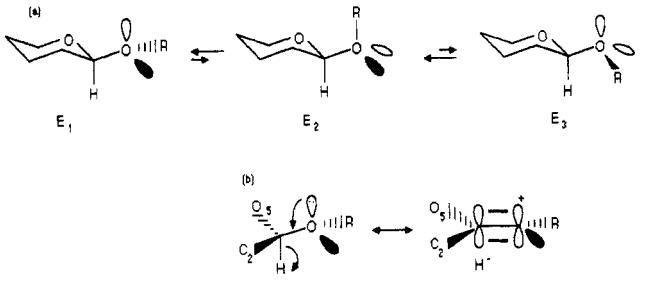

Figure 6.

from acetyl to propionyl or butyryl, H-1 and H-5 moved upfield and H-2 remained nearly unchanged.

Except for the carbon–hydrogen coupling constants for C-5, the ^{13}C data in Table II exhibit similar predictability. Of particular note is the trend for the C_1–H_1 couplings. Progressing from a polar solvent to a less polar solvent then to a larger acyl group results in a progressive decrease in $^1J_{C1,H1}$ values. In 1969, Perlin and Casu[10] reported that D-glucose enriched in carbon-13 showed $^1J_{C1,H1}$ values of 169 and 160 Hz for the α and β anomers, respectively. In addition, there are several reports of ca. 10-Hz differences in couplings for several anomeric pairs of pyranoses and derivatives, oligosaccharides, and polysaccharides.[11] These values are often taken as diagnostic of the configuration at these centers. For the case at hand, the trends in chemical shifts and in $^1J_{C1,H1}$ values are not readily explainable in terms of configurational changes at C-1. Currently, we believe these results can be rationalized in terms of the stereoelectronic effect of the exo oxygen (*exo*-anomeric effect).

Polysaccharides with a β configuration at C-1 can in principle adopt three conformations,[12] E_1, E_2, and E_3, about the C_1–O_{exo} bond (Figure 6a). Steric interactions and stereoelectronic effects will determine the relative conformer populations. Conformers E_1 and E_2 have one anomeric contribution whereas E_3 has none. On this basis, E_3 would be expected to contribute much less to the total conformer population relative to E_1 and E_2. E_1 has one less gauche interaction than does E_2 and for this steric reason should be of lower energy than E_2.

For the case of the triesters of cellulose, progressively increasing the size of the acyl group should increase the contribution of E_1. This change in conformer population would, in effect, provide an increase in orbital overlap between the electron pair of the exo oxygen and the antibonding orbital of the C_1–H_1 σ bond (Figure 6b). The change in orbital overlap is reflected, for example, in the ^1H NMR spectra of the esters by an upfield shift (increased electron density) for H-1 (vide supra). Conversely, changing to a more polar solvent[13] increases the contribution of E_2 to the conformer population and decreases orbital overlap between the exo oxygen and the C_1–H_1 σ bond. The resulting decrease in electron density at H-1 is reflected in the ^1H NMR spectra by a downfield shift for H-1 (vide supra).

Conclusion

By combining 2D NMR and resolution-enhancement techniques, we have provided the first unambiguous spectral assignment of cellulose esters **1**, **2**, and **3**. We find this combination to be a general and practical method for studying polysaccharides. By assignment of chemical shifts, identification of overlapping protons, and reduction of line width, interpretation of the spectra of polysaccharides can be made easier. This in turn can provide insight into the solution conformation of these important biopolymer derivatives. Further studies in this area are in progress and will be reported in due course.

Experimental Section

Materials. Cellulose (Placetate, I.T.T. Rayonier) was water activated before use by soaking it in water for 2 h followed by mechanical disruption of the fibers. The water was removed by vacuum filtration and exchanged with AcOH (five 300-mL portions). All other materials were used as commercially available.

Procedures. Reactions were routinely carried out under a nitrogen atmosphere and mechanical stirring was employed. Products were isolated by precipitation in water and dried at 0.3 Torr for several days.

Spectra. ^{13}C and ^1H NMR data were obtained on either a JEOL Model GX-270 NMR spectrometer (operating at 270 MHz for ^1H and 67.5 MHz for ^{13}C) or a JEOL Model GX-400 NMR spectrometer (operating at 400 MHz for ^1H and 100 MHz for ^{13}C). Sample tube sizes were 5 mm and 10 mm for ^1H and ^{13}C NMR, respectively. Chemical shifts are reported in parts per million from tetramethylsilane with $CDCl_3$ and DMSO-d_6 as internal references. For ^1H NMR, residual $CHCl_3$ was taken as 7.24 ppm and residual DMSO as 2.49 ppm. For ^{13}C NMR, the center peak of $CDCl_3$ was taken as 77.0 ppm and the center peak of DMSO-d_6 as 39.5 ppm. Splitting patterns are designated as singlet, s; doublet, d; triplet, t; quartet, q; and multiplet, m. Typical sample concentrations were 30 mg/mL for the ^1H NMR spectra and 100 mg/mL for ^{13}C NMR spectra.

The COSY[14] spectra were collected by using a 512 × 1024 data matrix size (more than necessary), and 48 transients were acquired for each t_1 value. Spectral widths of 1489 Hz were used in both dimensions. The spectra were processed by using a sine bell filtering function in both dimensions. Heteronuclear chemical shift correlation spectra[15] were recorded by using a 512 × 2048 data matrix size and 512 scans for each t_1 value. The carbon spectral window was 6265 Hz and the proton 1429 Hz. The delays were 3 and 2.2 ms.

Cellulose Triacetate (1). In a 2-L flask was placed 30 g of cellulose and 75 mL of AcOH (96 mL of AcOH was present from the exchange). To the heterogenous mixture was added a cooled solution (-50 °C) of 111 mL of acetic anhydride and 1 g of H_2SO_4. The mixture was stirred for 2.5 h at room temperature then warmed to 60 °C for 3.5 h before adding a solution of 1.2 g of $MgCO_3$ in 12 mL of AcOH. The solution was refluxed for 45 min then cooled to room temperature before adding 15 mL of water and 15 mL of AcOH. After stirring for 5 min, the solution was vacuum filtered and the product precipitated. The water was removed from the solids by decantation, 500 mL of water added, and the mixture placed in a steam bath for 1 h. The steam bath treatment was repeated 2 times. After the product was dried, 43.9 g of a white solid was isolated. Back-titration[1b] showed the degree of substitution to be 3.07.

Cellulose Tripropionate (2). A procedure similar to the one used for the preparation of **1** was used to prepare a propionate ester of cellulose (by ^{13}C NMR, esterification was incomplete). Full esterification was achieved by the following procedure: In a 100 mL flask were placed 2.0 g of cellulose propionate, 35 mL of dry CH_2Cl_2, and 4.3 mL of dry TEA. To the homogenous solution was added 0.56 g (3.8 mmol) of 4-pyrrolidinopyridine followed by 3.9 mL (30.7 mmol) of Pr_2O in one portion. After 28 h, the reaction mixture was washed with two 25-mL portions of water. The CH_2Cl_2 was removed in vacuo. The solids were taken up in acetone and the solution was poured into water. The resulting white solid was isolated by filtration. The dissolution and precipitation was repeated 2 times. After drying, 1.3 g of fully esterified material was obtained.

Cellulose Tributyrate (3). The same procedure used in the preparation of **2** was used to prepare 1.8 g of **3**.

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Registry No. CTA, 9012-09-3; CTB, 39320-16-6; CTP, 39320-19-9.

Supplementary Material Available: COSY spectra, C–H correlation spectra, and resolution-enhanced ^1H NMR spectra of CTA (**1**) (DMSO-d_6), CTP (**2**) ($CDCl_3$), and CTB (**3**) ($CDCl_3$)

(9 pages). Ordering information is given on any current masthead page.

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Solid-State Fluorine-19 Nuclear Magnetic Resonance Study of Fluorocarbon Polymers

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ABSTRACT: ^{19}F NMR at 338.7 MHz, with high-speed magic-angle spinning (MAS), has been used to study a number of fluorocarbon polymers. Systems studied were copolymers of vinylidene fluoride and hexafluoropropene, copolymers of vinylidene fluoride and chlorotrifluoroethene, and terpolymers of vinylidene fluoride, tetrafluoroethene, and hexafluoropropene. High-resolution spectra of all samples were obtained by using MAS speeds greater than 18 kHz. Structural assignments of chemical shifts in terms of five-carbon (pentad) sequences were made on the basis of solution-state studies. Sufficient resolution is obtained under high-speed MAS conditions to determine the relative concentration of each carbon pentad present. Monomer composition can also be determined from the ^{19}F MAS NMR data. Agreement with known compositions, when available, is good.

Introduction

Some of the initial applications of NMR spectroscopy to the determination of the structure of polymers was accomplished by using ^{19}F NMR on liquid samples.[1-4] A number of studies followed and led to a better understanding not only of the structure of polymers but also of the reaction rate constants governing the addition of particular monomers to a growing polymer chain.[5-18] A major advantage of ^{19}F NMR in polymer studies is the large chemical shift range for this nucleus. The effect of nearest and next-nearest neighbors on the chemical shift of a particular fluorine is readily measured.[3] Thus, it is possible to determine the number and type of monomer sequences present in a fluorocarbon polymer.[5-18] However, high-resolution ^{19}F NMR studies of polymers have been limited to solution-state spectra and have often employed low molecular weight polymers.

The need for a practical high-resolution technique for solid samples of these kinds of polymers is underscored by the fact that most known solvents must either be used at high temperature[14] or cause spectral overlap.[19] Furthermore, the ability to obtain spectra of undissolved polymers allows one to examine a polymer directly in the state in which its common structural applications depend.

^{19}F NMR measurements on solid samples using multiple-pulse methods[20] have yielded such parameters as the principal values of the chemical shift tensor,[21,22] but the chemical shift fine structure normally present in solution-state studies were not present in those studies. A high-resolution solid-state ^{19}F NMR study of fluoroapatite and fluorohydroxyapatite using magic-angle spinning (MAS) has appeared,[23] but successful ^{19}F MAS NMR studies of solid fluorocarbon polymers have not previously been published. This situation is probably a manifestation of the different characters of the anisotropic interactions present in the apatite and fluorocarbon polymer systems. For the apatite minerals high-resolution solid-state ^{19}F MAS NMR spectra can be obtained[23] by using moderate sample-spinning speeds (e.g., 3–5 kHz) because the dominant cause of line broadening is due to inhomogeneous interactions—chemical shift anisotropy and ^{19}F–^{19}F dipolar interactions between rather remote nuclei.[24] While the apatite spectra are complicated by the presence of spinning sidebands, isotropic chemical shifts can still be obtained.

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